**"State-to-state thermal/hyperthermal collision dynamics of atmospheric species"**
AFOSR F49620-97-1-0038

**Final report:**

Shot noise limited direct absorption IR laser methods have been used to study i) state-to-state reaction dynamics in crossed supersonic jets and ii) temperature dependent studies of OH + $O_3$ chemical chain reaction kinetics via flash kinetic spectroscopy. In this first area, state-resolved studies of F + $H_2$ scattering have now been completed from $E_{com}$ = 2.4 kcals/mole down to 0.30 kcals/mole, which by virtue of the high quantum state resolution in product detection have revealed contributions due to *non-adiabatic* reactions with spin orbit excited $F^*$ atoms. These methods have been extended to F + $CH_4$, where high resolution IR laser Dopplerimetry can be used to extract product state velocities and thus differential cross section information at the state-to-state level. Time resolved flash kinetic studies of the OH/$HO_2$/$O_3$ chemical chain reaction has been performed from 300K down to 190K, providing first access to temperature conditions relevant to accurate modeling of the lower stratosphere. Most recently, these methods have been extended to study "airglow" dynamics of highly rotationally excited OH(v,N) radicals formed from H+$O_3$ reactions.

These results are either published, in press, or submitted to the major journals in the field; the 17 papers resulting from work during this granting period are summarized below.

**Papers published, in press or submitted under the current granting period acknowledging AFOSR support**

1) Z.-Q. Zhao, W. B. Chapman and D. J. Nesbitt, "State-resolved differential scattering in open-shell collisions: Cl($^2P_{3/2}$) + HCl from high resolution IR laser Dopplerimetry," J. Chem. Phys. 104, 3555 (1996).

2) A. Schiffman, W. B. Chapman and D. J. Nesbitt, "State-to-state rotational energy transfer dynamics in crossed supersonic jets: A high resolution IR absorption method," J. Phys. Chem. 100, 3402 (1996).

3) M. J. Weida, J. M. Sperhac and D. J. Nesbitt, "Sublimation dynamics of $CO_2$ thin films: A high resolution diode laser study of quantum state-resolved sticking coefficients", J. Chem. Phys. 105, 749 (1996).

4) W. B. Chapman, A. Schiffman and D. J. Nesbitt, "Rotationally inelastic scattering in $CH_4$ + He, Ne and Ar: State-to-state cross sections via infrared laser absorption spectroscopy in crossed jets", J. Chem. Phys. 105, 3497 (1996).

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**14. ABSTRACT**

Shot-noise limited, direct absorption IR laser methods have been used to study (i) state-to-state reaction dynamics in crossed supersonic jets and (ii) temperature dependent studies of OH + $O_3$ chemical chain reaction kinetics via flash kinetic spectroscopy. In this first area, state-resolved studies of F + $H_2$ scattering have been completed from $E_{coll}$ = 2.4 kcals/mole down to 0.30 kcals/mole, which by virtue of the high quantum state resolution in product detection have revealed contributions due to *non-adiabatic* reactions with spin orbit excited F* atoms. These methods have been extended to F + $CH_4$, where high resolution IR laser Dopplerimetry can be used to extract product state velocities and thus differential cross section information at the state-to-state level. Time-resolved flash kinetic studies of the OH/$HO_2$/$O_3$ chemical chain reaction has been performed from 300 K down to 190 K, providing first access to temperature conditions relevant to accurate modeling of the lower stratosphere. These methods have been extended to study "airglow" dynamics of highly rotationally excited OH(v,N) radicals formed from H + $O_3$ reactions.

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5) D. J. Nesbitt and R. W. Field, "Vibrational energy flow in highly excited molecules: Role of Intramolecular Vibrational Relaxation (IVR)", invited review for the 100th anniversary of J. Phys. Chem. 100, 12735 (1996).

6) D. T. Anderson, S. Davis, T. S. Zwier and D. J. Nesbitt, "An intense slit discharge source of jet cooled molecular ions and radicals", Chem. Phys. Lett. 258, 207 (1996).

7) W. B. Chapman, M. J. Weida and D. J. Nesbitt, "State-to-state scattering of HF + He, Ne and Ar: Cross sections, Dopplerimetry and alignment studies via direct IR laser absorption in crossed supersonic jets", J. Chem. Phys. 106, 2248 (1997)

8) S. Davis, D. T. Anderson, G. Duxbury and D. J. Nesbitt, "Jet-cooled molecular radicals in slit supersonic discharges: Sub-Doppler IR studies of methyl radical", J. Chem. Phys. 107, 5661 (1997).

9) W. B. Chapman, B. W. Blackmon and D. J. Nesbitt, "State-to-state reactive scattering of F + $H_2$ in supersonic jets: Nascent rovibrational HF(v,J) distributions via direct IR laser absorption", J. Chem. Phys. 107, 8193 (1997).

10) A. Kulcke, B. W. Blackmon, W. B. Chapman, I. K. Kim and D. J. Nesbitt, "Time-resolved $O_3$ chemical chain reaction kinetics via high-resolution IR laser absorption methods", J. Phys. Chem. 102, 1965 (1998).

11) W. B. Chapman, Jr., B. W. Blackmon, S. Nizkorodov and D. J. Nesbitt, "Quantum state resolved reactive scattering of F + $H_2$ in supersonic jets: Nascent HF(v,J) rovibrational distributions via IR laser direct absorption methods", J. Chem. Phys. 109, 9306-9317 (1998)

12) W. B. Chapman, A. Kulcke, B. W. Blackmon and D. J. Nesbitt, "Rotationally inelastic scattering of jet cooled $H_2O$ with Ar: State-to-state cross sections and rotational alignment effects", J. Chem. Phys. 110, 8543 (1999).

13) S. A. Nizkorodov, W. W. Harper and D. J. Nesbitt, "State-to-state reaction dynamics in crossed supersonic jets: threshold evidence for non-adiabatic channels in F + $H_2$", Faraday Disc. 113, 107 (1999).

14) J. R. Fair and D. J. Nesbitt, "Dynamics of Collisional Alignment in Supersonic Expansions: Trajectory Studies of He + CO, $O_2$ and $CO_2$", J. Chem. Phys. 111, 6821 (1999).

15) S. A. Nizkorodov, W. W. Harper, W. B. Chapman, B. W. Blackmon and D. J. Nesbitt, "Energy dependent cross sections and non-adiabatic reaction dynamics in $F(^2P_{3/2}, ^2P_{1/2})$ + n-$H_2 \rightarrow$ HF(v,J) + H", J. Chem. Phys. 111, 8404 (1999).

16) S. A. Nizkorodov, W. W. Harper, B. W. Blackmon and D. J. Nesbitt, "Temperature dependent kinetic studies of the $OH/HO_2/O_3$ chain reaction by time resolved high resolution laser absorption spectroscopy", J. Phys. Chem (in press).

17) W. W. Harper, S. A. Nizkorodov, and D. J. Nesbitt, "Quantum state-resolved reactive scattering of $F + CH_4 \rightarrow HF(v,J) + CH_3$: Nascent HF(v,J) product state distributions", J. Chem. Phys. (submitted).

**Prizes, awards, and fellowships received during the current granting period**

Earle K. Plyler Prize, 1997
William F. Meggers Award, 1999
Alexander von Humboldt Fellowship, 1999

**Invited talks during the current AFOSR granting period**

"Watching molecules touch: New perspectives via high resolution infrared lasers", Reilly Lectures, Department of Chemistry, Notre Dame University, South Bend, IN, February 3, 1997.

"Probing intermolecular potentials: hydrogen bonds, helicopters and heat baths", Reilly Lectures, Department of Chemistry, Notre Dame University, South Bend, IN, February 4, 1997.

"State-resolved studies of transient species: radicals, ions and ozone chain chemistry", Reilly Lectures, Department of Chemistry, Notre Dame University, South Bend, IN, February 5, 1997.

"Unimolecular dynamics in molecular clusters: Hydrogen bonding, 3-body forces and open shell species", Plyler Award Lecture, American Physical Society Meeting, Kansas City, MO, March 20, 1997.

"State-to-state dynamics with high resolution IR lasers: From hydrogen bonded clusters to hydrocarbon radicals", Department of Chemistry, University of Minnesota, Minneapolis, MN, April 7, 1997.

"Intermolecular orientation/alignment effects in unimolecular photolysis of clusters", American Chemical Society, San Francisco, CA, April 17, 1997.

"High resolution Inter- and Intramolecular Spectroscopy of Hydrogen Bonded Species: Benchmark Tests of Ab-initio and Semiempirical Theory", NATO Advanced Studies Institute on Hydrogen Bonding, Heraklion, Crete, Greece, June 25, 1997.

"Large Amplitude Motion, Tunneling and Intramolecular Energy Flow in Hydrogen Bonded Clusters", NATO Advanced Studies Institute on Hydrogen Bonding, Heraklion, Crete, Greece, June 27, 1997.

"IR Laser Studies of Molecular Alignment and Reaction Dynamics", Symposium on Interactions of Oriented Molecules, Center for Interdisciplinary Research (ZiF), University of Bielefeld, Bielefeld, Germany, July 2, 1997.

"Chemistry is fun!", CU Wizards Science Outreach Program, Department of Chemistry, University Colorado, Boulder, CO, September 27, 1997.

"High resolution IR laser studies in slit supersonic discharges: Jet cooled hydrocarbon radicals and molecular ions", 1997 Optical Society of America Annual Meeting, Long Beach, CA, October 14, 1997.

"Spectroscopy and dynamics of open and closed shell clusters", Gordon Conference on Molecular and Ionic Clusters, Ventura, CA, January 4, 1998.

"Clusters, radicals and nanostructures", Department of Chemistry, Baylor University, Waco, TX, February 20, 1998.

"From clusters to chemical reactions: State-resolved dynamics via high resolution IR laser methods", Department of Chemistry, UCL A, Los Angeles, CA, March 9, 1998.

"Clusters, radicals and nanostructures", Department of Chemistry, Marquette University, Milwaukee, WI, April 7, 1998.

"Clusters, radicals and nanostructures", Department of Chemistry, Carroll College, Waukesha, WI, April 7, 1998.

"Watching molecules touch: From IR laser studies of hydrogen bonding to atomic force microscopy", Department of Chemistry, Carthage College, Milwaukee, WI, April 8, 1998.

"Watching molecules touch: From IR laser studies of hydrogen bonding to atomic force microscopy", Department of Chemistry, Beloit College, Beloit, WI, April 8, 1998.

"State-resolved dynamics in water via high resolution IR laser methods: clusters, collisions and photochemistry", International Conference on water in the gas phase, University of Marne-la-Vallee, Paris, France, June 22, 1998.

"From clusters to chemical reactions: State-resolved dynamics via high resolution IR laser methods", Department of Chemistry, University de Paris-Sud, Orsay, France, June 25, 1998.

"From clusters to chemical reactions: state-resolved dynamics via high resolution IR laser methods", Institute for Theoretical Chemistry, University of Stuttgart, Stuttgart, Germany, June 30, 1998.

"State-to-state collision dynamics in crossed supersonic jets: Probing reactions with high resolution infrared lasers", University of Goettingen and Max Planck Institute fuer Stroemungsforschung, Goettingen, Germany, July 2, 1998.

"Large amplitude vibrational motion in hydrocarbon radicals and $H_2$-containing clusters", workshop on Quantum Dynamics of Coupled Large Amplitude Vibrations in Floppy Molecules, Clusters and Biomacromolecules, Telluride Summer Research Center, Telluride, CO, July 28, 1998.

"Chemistry all around us", CU Wizards Science Outreach Program, Department of Chemistry, University Colorado, Boulder, CO, December 26, 1998.

"Watching molecules touch: From high resolution spectroscopy of clusters to atomic force microscopy", Departments of Physics and Chemistry, Wesleyan University, Middletown, CT, January 29, 1999.

"State-to-state reaction dynamics in crossed supersonic jets", Department of Physics, University of Connecticut, Storrs, CT, January 30, 1999.

"Clusters, radicals and nanoparticles: From state-to-state reactions dynamics to near field microscopy", Department of Chemistry, U. C. San Diego, La Jolla, CA, February 23, 1999.

"High resolution full and half collision studies of intermolecular potentials", UK Collaborative Computational Project on Heavy Particle Dynamics (CCP6), University of Aberdeen, Aberdeen, Scotland, April 13, 1999.

"Chemical physics with lasers: From state-to-state collision dynamics to single molecule spectroscopy", Department of Physics and Astronomy, University of Delaware, Newark, DE, April 21, 1999.

"Collisional Dynamics of Rotational Alignment", Molecular Aspects of Gas Dynamics, National Academy, Perugia, Italy, June 19, 1999.

"Experimental/theoretical studies of state-to-state collision phenomena: Rotational alignment and non-adiabatic reaction dynamics", Conference on Molecular Energy Transfer XVI, Assisi, Italy, June 22, 1999.

"State-to-state reaction dynamics in crossed supersonic jets: threshold evidence for non-adiabatic channels in F + $H_2$", Faraday Disc., Leeds, UK, July 6, 1999.

"From spectroscopy of radical spectroscopy to near field microscopy", Department of Chemistry, University of Birmingham, Birmingham, UK, July 8, 1999.

"Chemical physics with lasers: From state-to-state collision dynamics to single molecule microscopy", Department of Chemistry, Oxford University, July 12, 1999.

"State-to-state reactive scattering in crossed supersonic jets", Department of Chemistry, University College London, London, UK, July 14, 1999.

"Non-adiabatic reaction dynamics in F + n-$H_2$ from IR laser based state-to-state reactive scattering studies", American Chemical Society (218$^{th}$ National Meeting), New Orleans, LA, August 23, 1999.

"Single particle microscopy above and below the diffraction limit", Optical Society of America, Santa Clara, CA, September 28, 1999.

"Chemical physics with lasers: From slit jet discharges to single molecule spectroscopy", Department of Chemistry, University of Wisconsin, Madison, WI, October 26, 1999.

"Where Chemistry meets Physics", CU Wizards Science Outreach Program, Department of Chemistry, University Colorado, Boulder, CO, October 30, 1999.

"From state-to-state reaction dynamics to single molecule microscopy", Department of Chemistry, University of Maryland, College Park, MD, November 11, 1999.

"Chemical dynamics with a twist: From state-resolved reactions in supersonic jets to single molecule microscopy", Department of Chemistry, University of Southern California, Los Angeles, CA, January 10, 2000.

"Chemical kinetics with a twist: From state-to-state reaction dynamics to single molecule microscopy", Department of Chemistry, University of Arizona, Tuscson, AZ, January 24, 2000.

"Microscopy at and below the diffraction limit via resonant scattering and laser induced fluorescence: Recent progress from apertureless NSOM", American Physical Society, Minneapolis, MN, March 21, 2000.

"Probing quantum state to state dynamics: From clusters to chemical reactions", American Chemical Society (219th national Meeting), San Francisco, CA, March 26, 2000.

"From Single Collisions to Single Molecules", Institute for Physical Chemistry, University of Goettingen, Goettingen, Germany, April 13, 2000

"Spectroscopy above and below the diffraction limit", Max Planck Institute for Biophysical Chemistry, Goettingen, Germany, April 28, 2000.